ET110

Source Apportionment of Regional Air Pollutant Fallout using Trace Element/Common Ion Measurements and Multi-Variate Receptor Modeling Methods

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ABSTRACT

We are developing a new approach to characterize and source-apportion air pollutant fallout on a region-wide scale to enhance the INEEL's capability to meet regulatory permitting requirements for existing and future EM-waste treatment facilities. The approach uses multivariate correlations (scatter plots, principal component analysis [PCA], and principal component regression [PCR]) of trace element/common ion measurements in snow (a good fallout scavenger) to: 1) identify the major fallout sources in the region and 2) predict the relative contribution to total fallout at a sampling location from the different sources. In FY01, we collected more than 250 INEEL and regional snow samples and analyzed them in triplicate using inductively-coupled plasma mass spectrometry (ICPMS) and ion chromatography (IC). Thirty-nine trace elements and 9 common ions were positively identified in most samples. The results have been processed, plotted on regional maps, and plotted as bivariate element scatter plots. In FY02, we will perform PCA/PCR to identify regional fallout sources and develop a model to predict the fractional contributions to fallout from these sources at any given sampling location in the region.

FY01 TECHNICAL OBJECTIVES

- Performed comprehensive monthly (Dec-Mar) snow sampling on the INEEL and Eastern Snake River Plain (ESRP). Analyzed the samples for a broad suite of trace elements and common ions using ICPMS and IC. Reduced the analytical data to a reliable and useable format using instrument detection limits, lab and field blanks, and instrument standards.
- Performed initial data exploratory analysis - identified key fallout elements, their region-wide spatial variability, and site-specific correlations among elements using the software, Pirouette®.

TECHNICAL NARRATIVE

The ultimate objective of this research is to develop a new method to characterize and source-apportion air pollutant fallout across the ESRP airshed. Three major tasks are: 1) ultra-low trace measurements of a broad suite of elements and common ions in snow (an efficient scavenger of fallout), 2) use of multivariate statistical techniques to identify key combinations of fallout elements that characterize specific major sources throughout the region, and 3) development of a multivariate model that can be used to predict the fractional contribution of a particular source to the total fallout at any sampling site. These analyses will be done using regional plots of individual element concentrations, bivariate scatterplots of elements, principal component analysis (PCA), and principal component regression (PCR).

<u>Need</u>: Regulatory permitting and stakeholder acceptance of important waste treatment projects at the INEEL (e.g., AMWTP incinerator, NWCF calciner) have been impacted in the past by our inability to provide accurate predictions of long-range atmospheric transport of pollutants and by our general lack of scientific understanding of air pathway transport. A better understanding of source-specific fallout patterns (separating individual source contributions in the soup) is needed to facilitate acceptance of current and future waste treatment operations. Current monitoring methods measure only a few pollutants at few monitoring sites, often cannot differentiate one source from another, and often do not have the sensitivity to detect very low levels of contaminants that may still contribute to risk. Current modeling methods use relatively simple transport algorithms that typically only provide order-of-magnitude estimates and have not been validated in this region. This research will also contribute to DOE's long-term stewardship efforts by providing information on INEEL source contributions to region-wide surface buildup of contaminants.

<u>Accomplishments</u>:

1. <u>Sampling</u>. We obtained 250 snow samples on a 5-km radius grid around INTEC (64 locations) and at nine ESRP background sites surrounding the ESRP. Triplicate samples were normally taken using ultra-clean sampling techniques. The INTEC grid sites were sampled twice (Jan/Feb), and the background sites were sampled four times (Dec through March). Separate samples were taken for new (top-layer) snow and old (underlying) snow.

2. Lab Analysis. Each sample was analyzed in triplicate using ICPMS and IC at the US Geological Survey (USGS) Branch of Regional Research (BRR) in Boulder, CO. Mercury and total organic carbon were analyzed at the USGS Wisconsin District Mercury Research Laboratory (WDMRL). The analyses identified 39 elements and 9 common ions, providing more than 30,000 variables for statistical analyses. The total analytical cost for these analyses was $9,000.
3. Data Processing and QA/QC. Outliers were identified, lab replicates averaged, and lab detection limits modified for significant field blank detection. Most of the ICPMS data has been processed to date.
4. Regional Spatial Analysis. Individual trace element results were plotted as concentration isopleths on regional maps (using Surfer® Kriging and contouring software) to understand spatial variability (38 plots). These results show relatively high Be, Cu, and Zn signals near INTEC, a Bi signal at Camas, a Pb signal from Idaho Falls, and Se, Cd, Tl, Er, and U signals from Pocatello (Figure 1).

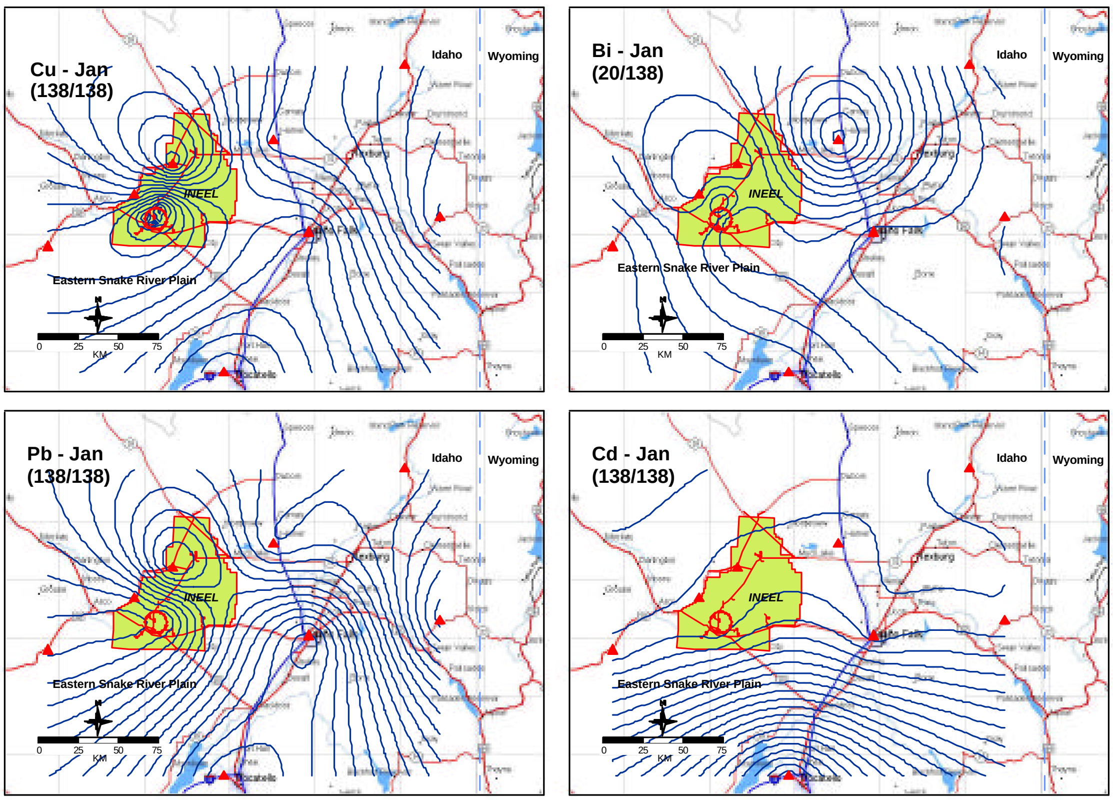

Figure 1. Examples of trace element (Cu, Bi, Pb, Cd) spatial trends in region-wide fallout.

5. Pirouette® Exploratory Analysis. Most air pollutant sources emit trace element combinations that are characteristic to their specific source type. As a first step (prior to PCA), we examined element correlations using Pirouette® scatterplots arrays (multiplots). Separate analyses were made with the following categories (class variables): 1) by sampling month, 2) by general sample site location (INTEC grid vs. background site), 3) by wind vector quadrants (downwind NE, downwind SW, cross-wind), and 4) by distance from the INTEC main stack (1, 2, 3, and 5-km distance). The class variables are color-coded which provides rapid visual identification of element correlations. These plots (examples in Figure 2) indicate: 1) no large difference in element correlations by month (indicating that all data can be combined for further analysis), 2) near perfect correlations of the rare earth and actinide elements (suggesting a single source for these), 3) large differences in element correlations between the Pocatello samples and all other locations (Al/V, Pr/La, Ce/La, Sm/Y), and 4) some smaller identifiable differences between grid and background site correlations (Al/Li, Mn/Li, Eu/La).

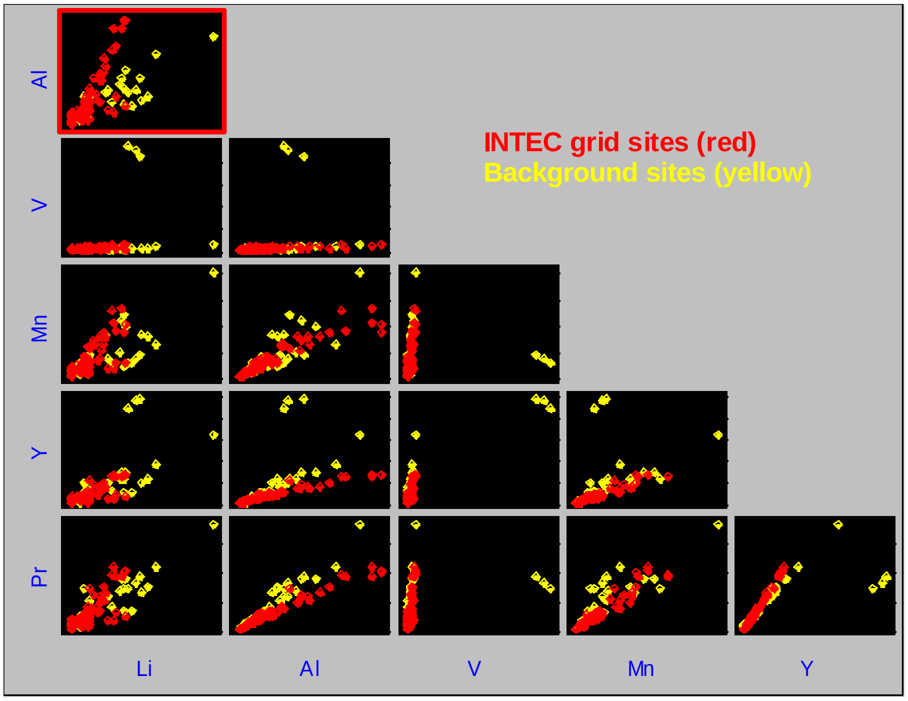

Figure 2. Bivariate scatter plot array of trace element concentrations in fallout on the INEEL (red) and at regional background sites (yellow). There are over 1,000 possible combinations of these element relationships from the 39 trace elements and 9 common ions detected in the samples.

FY02 Plans: 1) Analyze remaining FY01 sampling data (primarily common ions), 2) perform limited snow sampling (25% FY01 effort) to build data base and capture year-to-year changes in INEEL/regional emissions, 3) advance INEEL skills in data exploratory analysis (Pirouette® training for INEEL PIs), 4) develop and validate PCA model, 5) publish/present results, and 6) develop INEEL operational applications and funding base.

BUISINESS DEVELOPMENT OPPORTUNITIES
This research will develop a new measurement-based method to reliably predict the relative contributions of major regional source categories (INEEL/others) to air pollutant fallout at any location throughout the ESRP. If successful, it will significantly enhance the INEEL's capabilities in environmental monitoring and assessment, reduce the cost and time needed for regulatory permitting of INEEL waste treatment facilities, and improve stakeholder understanding of the relative impacts of the INEEL in the region.

Follow-on operational funding will be requested in an FY02 Detailed Work Plan (DWP) proposal to Environmental Management (EM) and the High Level Waste Program as part of their FY02-05 waste characterization and permitting activities. As part of this effort, a presentation will be made to DOE-ID environmental compliance managers, five of whom previously expressed their written support for this research. The funding request will be dependent upon the FY02 mid-year results from this work but is currently estimated to be $200K/year.

The research is expanding INEEL collaboration with a previously unexplored federal research agency—the USGS Branch of Regional Research, Central Region (BRR, CR). This nationally-recognized research lab can provide the INEEL with extremely cost-effective laboratory analyses for future research needs. Also, this research is closely connected with on-going INEEL mercury research, which will be funded by the HLW Program in FY02-03. The mercury work has resulted in two external proposals which have included the INEEL as a collaborator: 1) a National Atmospheric Deposition Program (NADP) proposal with the USGS ($72K) and 2) a U.S. Environmental Protection Agency (EPA) Science-to-Achieve-Results (STAR) proposal with the University of Wisconsin-Madison ($900K).